

FORM PTO-1390
(REV. 9-2001)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

M&M-048-USA-PCT

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/019433

INTERNATIONAL APPLICATION NO.
PCT/JP00/05694

INTERNATIONAL FILING DATE
August 24, 2000

PRIORITY DATE CLAIMED
August 27, 1999

TITLE OF INVENTION

Adhesive Composition And Joining Method Utilizing the Adhesive Composition

APPLICANT(S) FOR DO/EO/US

Takeo Kuroda, Hiroji Fukui and Hideaki Ishizawa

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☒ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: **Claim For Priority
English Translation of the Amendment Under
Article 11**

U.S. APPLICATION NO. If known (see 37 CFR 1.51)

10/019433

INTERNATIONAL APPLICATION NO.
PCT/JP00/05694

ATTORNEY'S DOCKET NUMBER

M&M-048-USA-PCT

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO..... \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	19 - 20 =	-0-	x \$18.00	\$ -0-
Independent claims	3 - 3 =	-0-	x \$84.00	\$ -0-

MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$280.00 \$

TOTAL OF ABOVE CALCULATIONS = \$ 890.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

\$

SUBTOTAL = \$ 890.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE = \$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

TOTAL FEES ENCLOSED = \$ 930.00Amount to be
refunded: \$

charged: \$

- a. ☒ A check in the amount of \$ 930.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 20-1424 A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

TOWNSEND & BANTA
Suite 500, #50028
1225 Eye St., N.W.
Washington, D.C. 20005

Phone: (202) 682-4727

SIGNATURE

Donald E. Townsend

NAME

22,069

REGISTRATION NUMBER

M&M-048-USA-PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of
T. Kuroda, et al.

International Application No.: PCT/JP00/05694

International Filing Date: August 24, 2000

Title: Adhesive Composition And Joining Method Utilizing The
Adhesive Composition

PRELIMINARY AMENDMENT

BOX PCT

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

After assigning a serial number to the above-captioned application and before calculating the fee, please undertake the following changes:

IN THE CLAIMS

Please cancel claims 2, 4 and 9, and substitute the amended claims 1, 3, 5-8 and 10 for the original claims 1, 3, 5-8 and 10 as follows:

1. (Amended) An adhesive composition (A) a compound having at least two hydrolysable silyl groups in a molecule;

(B) a compound which initiates crosslinking of the compound (A);

(C) a compound having a polymerizable group in a molecule;

(D) a compound which is activated by irradiation to initiate polymerization of the polymerizable group in the compound (C); and

(E) a thixotropic agent

wherein:

said adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps, conversions of the compounds (A) and (C) are in the range of 10 - 70 %, the composition immediately after its exposure to the active energy radiation has a dynamic shear modulus in the range of $10^5 - 10^7$ Pa; and

the conversions of the compounds (A) and (C) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C are in the range of 50 - 100 %, and after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of $10^5 - 10^9$ Pa.

3. (Amended) The adhesive composition as recited in claim 1, wherein the conversions of the compounds (A) and (C) immediately after exposure of the adhesive composition to the active energy radiation are in the range of 10 - 70 % and the adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and the conversions of the compounds (A) and (C) after exposure of the

adhesive composition to the active energy radiation and subsequent 12-hour aging at 25 °C is in the range of 50 - 100 %.

5. (Amended) The adhesive composition as recited in claim 1, wherein the hydrolyzable silyl group in the compound (A) is a alkoxysilyl group, and the compound (A) is a compound containing the alkoxysilyl group substituted in a polymer selected from polyalkylene glycols and polyolefins.

6. (Amended) The adhesive composition as recited in claim 1, wherein the polymerizable group in the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

7. (Amended) The adhesive composition as recited in claim 1, wherein the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

8. (Amended) The adhesive composition as recited in claim 1, wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

10. (Amended) A method of joining members comprising, in sequence, applying the adhesive composition as recited in claim 1 to one of the members, exposing a top surface of the applied adhesive composition layer to an active energy radiation, and combining the one member with the other member.

Please add new claims 11-21 as follows:

11. An adhesive composition comprising:

a compound (X) having a crosslinkable or polymerizable group;
and

a compound (Y) which is activated when exposed to an active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X) wherein:

a conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation does not exceed 30 %, and the composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and

a conversion of the compound (X) after exposure of the adhesive composition to the active energy radiation and subsequent 12-hour aging at 25 °C is in the range of 50 - 100 %.

12. The adhesive composition as recited in claim 3, wherein the hydrolyzable silyl group in the compound (A) is a alkoxysilyl group, and the compound (A) is a compound containing the alkoxysilyl group substituted in a polymer selected from polyalkylene glycols and polyolefins.

13. The adhesive composition as recited in claim 3, wherein the polymerizable group in the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

14. The adhesive composition as recited in claim 5, wherein the polymerizable group in the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

15. The adhesive composition as recited in claim 3, wherein the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

16. The adhesive composition as recited in claim 5, wherein the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

17. The adhesive composition as recited in claim 7, wherein the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

18. The adhesive composition as recited in claim 3, wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

19. The adhesive composition as recited in claim 5, wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

20. The adhesive composition as recited in claim 6, wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

21. The adhesive composition as recited in claim 7, wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

REMARKS

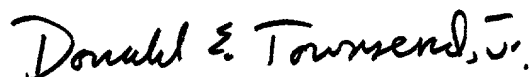
The amendments to Claims 1, 3, 5-8 and 10, and the addition of new claims 11-21, are made to eliminate the multiple dependencies, to place the claims in proper U.S. format, and to conform the claims to the claims as amended in the international application in the Amendment under Article 11 dated April 12, 2001. The present amendment is deemed not to add new matter. Claims 1, 3, 5-8 and 10-21 are in the application.

It is respectfully submitted that this application is now in condition for examination on the merits and early action and allowance thereof is accordingly respectfully requested.

Respectfully submitted,



Donald E. Townsend
Reg. No. 22,069



Donald E. Townsend, Jr.
Reg. No. 43,198

Date: December 31, 2001

TOWNSEND & BANTA
1225 Eye Street, N.W.
Suite 500, #50028
Washington, D.C. 20005
(202) 682-4727

MARKED-UP VERSIONS OF AMENDED CLAIMS 1, 3, 5-8 AND 10:

1. (Amended) An adhesive composition [characterized as containing a compound (X) having a crosslinkable or polymerizable group and a compound (Y) which is activated when exposed to an active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X)]

(A) a compound having at least two hydrolysable silyl groups in a molecule;

(B) a compound which initiates crosslinking of the compound (A);

(C) a compound having a polymerizable group in a molecule;

(D) a compound which is activated by irradiation to initiate polymerization of the polymerizable group in the compound (C); and

(E) a thixotropic agent

wherein:

said adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps, conversions of the compounds (A) and (C)[; a conversion of the compound (X)] immediately after exposure of the adhesive composition to the active energy radiation [does not exceed] are in the range of 10 - 70 %, the composition immediately after its exposure to the active energy radiation has a dynamic shear modulus in the range of 10^5 - 10^7 Pa; and [a conversion of the compound (X)]

the conversions of the compounds (A) and (C) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C [is] are in the range of 50 - 100 %[,], and after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of 10^5 - 10^9 Pa.

3. (Amended) The adhesive composition as recited in claim 1, [characterized in that the conversion] wherein the conversions of the [compound (X)] compounds (A) and (C) immediately after exposure of the adhesive composition to the active energy radiation are in the range of 10 - 70 % [does not exceed 30 %] and the adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and

the [conversion] conversions of the [compound (X)] compounds (A) and (C) after exposure of the adhesive composition to the active energy radiation and subsequent 12-hour aging at 25 °C is in the range of 50 - 100 %.

5. (Amended) The adhesive composition as recited in claim [4] 1, [characterized in that] wherein the hydrolyzable silyl group in the compound (A) is a alkoxysilyl group, and the compound (A) is a compound containing the alkoxysilyl group substituted in a polymer selected from polyalkylene glycols and polyolefins.

6. (Amended) The adhesive composition as recited in claim [4 or 5] 1, [characterized in that] wherein the polymerizable group in

the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

7. (Amended) The adhesive composition as recited in [any one of claims 4-6] claim 1, [characterized in that] wherein the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

8. (Amended) The adhesive composition as recited in [any one of claims 4-7] claim 1, [characterized in that] wherein the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

10. (Amended) A method of joining members [characterized as] comprising, in sequence, applying the adhesive composition as recited in [any one of claims] claim 1[-9] to one of the members, exposing a top surface of the applied adhesive composition layer to an active energy radiation, and combining the one member with the other member.

DOCKET NO. M&M-048-USA-PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

T. Kuroda, et al.

Serial No.: Corresponding to PCT/JP00/05694
filed August 24, 2000

Filed: Concurrently herewith

For: Adhesive Composition And Joining Method
Utilizing The Adhesive Composition

CLAIM FOR PRIORITY

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

Sir:

The benefit of the filing dates of the following prior foreign application filed in Japan is hereby requested for the above identified application and the priority provided in 35 U.S.C. 365 is hereby claimed:

Japanese patent application No. 11/241599 filed August 27, 1999.

In support of this claim, a certified copy of said original foreign application was filed with the International Bureau on

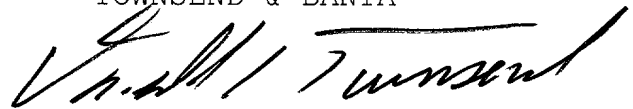
DOCKET NO. M&M-048-USA-PCT

September 27, 2000 as evidenced by form PCT/IB/304, which is attached.

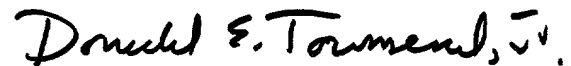
It is requested that the file of this application be marked to indicate that the requirements of 35 U.S.C. 365 have been fulfilled and that the Patent and Trademark Office kindly acknowledge receipt of these documents.

Respectfully submitted,

TOWNSEND & BANTA



Donald E. Townsend
Reg. No. 22,069



Donald E. Townsend, Jr.
Reg. No. 43,198

TOWNSEND & BANTA
1225 Eye Street, N.W.
Suite 500, #50028
Washington, D.C. 20005
(202) 682-4727

Date: December 31, 2001

AMENDMENT

(Under Article 11 of Japanese Law Concerning
International Applications, etc. Pursuant to PCT)

To : Director General of the Patent Office

1. Identification of the International Application

PCT/JP00/05694

2. Applicant

Name : SEKISUI CHEMICAL CO., LTD.

Address : 4-4, Nishitemma 2-chome, Kita-ku,
Osaka-shi, Osaka 530-8565 Japan

Country of nationality : Japan

Country of residence : Japan

3. Agent

Name : (8659) Patent Attorney MIYAZAKI Chikara

Address : Nishimura Bldg., 6-5,
Tanimachi 1-chome, Chuo-ku, Osaka-shi,
Osaka 540-0012 Japan

4. Item to be Amended

Claims

5. Contents of the Amendment

(1) Claim 1 is amended by combining subject matters of claims 2, 7 and 9.

(2) Claim 2 is deleted.

(3) Claim 3 is amended as dependent from claim 1 and amended to conform to the amendment of claim 1.

(4) Claim 4 is deleted.

(5) Dependency of claims 5 - 8 are amended.

(6) Claim 9 is deleted.

(7) Dependency of claim 10 is amended.

(8) Claim 11 directed to the same subject matter of original claim 3 is added.

6. List of Attached Documents

New pages of claims: pages 38, 38/1, 39 and 39/1

C L A I M S

1. (Amended) An adhesive composition characterized as containing:

5 (A) a compound having at least two hydrolyzable silyl groups in a molecule;

(B) a compound which initiates crosslinking of the compound (A);

10 (C) a compound having a polymerizable group in a molecule;

(D) a compound which is activated by irradiation to initiate polymerization of the polymerizable group in the compound (C); and

(E) a thixotropic agent

15 wherein:

said adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps, conversions of the compounds (A) and (C) immediately after exposure of the adhesive composition to an active energy radiation are in the range of 10 - 70 %, the composition immediately after its exposure to the active energy radiation has a dynamic shear modulus in the range of 20 $10^5 - 10^7$ Pa; and

the conversions of the compounds (A) and (C) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C are in the 25

range of 50 - 100 %, and after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of 10^5 - 10^9 Pa.

2. (Deleted)

3. (Amended) The adhesive composition as recited in claim 1, characterized in that the conversions of the compounds (A) and (C) immediately after exposure of the adhesive composition to an active energy radiation are in the range of 10 - 70 % and the adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and

the conversions of the compounds (A) and (C) after exposure of the adhesive composition to the active energy radiation and subsequent 12-hour aging at 25 °C are in the range of 50 - 100 %.

4. (Deleted)

(Blanked below)

5. (Amended) The adhesive composition as recited in claim 1 or 3, characterized in that the hydrolyzable silyl group in the compound (A) is a alkoxysilyl group, and the compound (A) is a compound containing the alkoxysilyl group substituted in a polymer selected from polyalkylene glycols and polyolefins.

6. (Amended) The adhesive composition as recited in any one of claims 1, 3 and 5, characterized in that the polymerizable group in the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

7. (Amended) The adhesive composition as recited in any one of claims 1, 3, 5 and 6, characterized in that the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

8. (Amended) The adhesive composition as recited in any one of claims 1, 3, 5, 6 and 7, characterized in that the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

9. (Deleted)

10. (Amended) A method of joining members characterized as comprising, in sequence, applying the adhesive

composition as recited in any one of claims 1, 3 and 5 - 8 to one of the members, exposing a top surface of the applied adhesive composition layer to an active energy radiation and combining the one member with the other member.

5 11. (Added) An adhesive composition characterized as containing:

 a compound (X) having a crosslinkable or polymerizable group; and

 a compound (Y) which is activated when exposed to an
10 active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X) wherein:

 a conversion of the compound (X) immediately after
 exposure of the adhesive composition to the active energy
15 radiation does not exceed 30 %, and the composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and

 a conversion of the compound (X) after exposure of the
 adhesive composition to the active energy radiation and
 subsequent 12-hour aging at 25 °C is in the range of 50 -
20 100 %.

(Blanked below)

S P E C I F I C A T I O N

ADHESIVE COMPOSITION AND JOINING METHOD UTILIZING THE
ADHESIVE COMPOSITION

5

TECHNICAL FIELD

This invention relates to an adhesive composition which is flowable in ordinary state, shows a spreadable viscosity, provides temporary bonding or fixing when its cohesion is improved by short-time exposure to an active energy radiation, and reaches a final bonding power when subjected to crosslinking or polymerization, and also to a joining method utilizing the adhesive composition.

BACKGROUND ART

In recent years, adhesives have come into wide-spread use in the fields of architecture and building materials for their superior productivity and workability. With the development of factory-produced housing or the like, there is an increasing need for adhesives which suit high-speed production of building components on assembly lines.

In Japanese Patent Laying-Open No. Sho 56-67366, an adhesive composition is proposed which contains a compound having a hydrolyzable silyl group such as an alkoxysilyl and cures in the presence of moisture or the like. This adhesive composition exhibits superior impact resistance and

creep resistance after it has been cured. Accordingly, its use at parts (e.g., joints between tiles or wall members) of a house that receive continuous loads has been investigated and actually practiced in building and construction sites.

5 However, due to the tendency to cure in the presence of moisture in the air, this adhesive composition, if designed to have a fast-curing property adapted for use on such an assembly line, has a shorter pot life and is thus prevented from residing on an applicator for extended period of time, 10 which has been a problem. On the other hand, if a design is made to extend a pot life of the composition, curing thereof is retarded. In such a case, an appropriate measure must be taken to hold components in positions. In addition, the composition must be aged until it completes curing.

15 In the meantime, photocurable compositions have been conventionally proposed (for example, in Japanese Patent Laying-Open No. Sho 63-139969) which are caused to cure by short-time exposure to a radiation. The application of such photocurable compositions to photo-curable inks, varnishes, 20 coating materials or adhesives has also been proposed. Since photocurable adhesives incorporating such photocurable compositions show fast-curing properties, a sufficiently long pot life can be insured simply by shielding a light that otherwise sensitizes them. Accordingly, the use as in- 25 line adhesives has been proposed. However, the photocurable

adhesives are generally irradiated after application thereof and following combination of adherends. This has prevented application of such photocurable adhesives to building and construction materials through which substantially no light
5 can pass.

Also, curable compositions containing, in combination, a compound containing the aforementioned hydrolyzable silyl group and a photocurable substance have been proposed (for example, in Japanese Patent Laying-Open Nos. Sho 55-36241
10 and Hei 8-325466) for the purposes of improving stain resistance, dust resistance, tack and weather resistance of cured surfaces when they are used as building sealants. It has been however difficult to rapidly develop fast-curing and cohesive properties by short-time irradiation.

15 This invention is directed toward solving the above-described problems and its object is to provide an adhesive composition which is flowable in ordinary state, has a spreadable viscosity, has a long pot life, develops cohesion by short-time irradiation, eliminates the need of temporary
20 bonding and fixing procedures and exhibits superior impact resistance, creep resistance and other properties after it has been cured, and a joining method utilizing the adhesive composition.

25 DISCLOSURE OF THE INVENTION

5 A first invention of this application is an adhesive composition characterized as containing a compound (X) having a crosslinkable or polymerizable group and a compound (Y) which is activated when exposed to an active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X), wherein the composition has a viscosity at 25 °C of 1 - 10,000,000 cps, a conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation does not exceed 70 %, a conversion of the compound (X) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C is within the range of 50 - 100 %, and after exposure to the active energy radiation and following 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of 10^5 - 10^9 Pa.

20 Prior to exposure to the active energy radiation, the adhesive composition in accordance with the first invention is stored under a light-shielded or dehumidified condition so that crosslinking or polymerization of the compound (X) is prevented. That is, the compound (X) undergoes little change to show suitable flowability in ordinary state. This eases application of the composition onto various types of adherends by hands or spreaders conventionally known in the

art.

The compound (Y) undergoes rapid decomposition upon exposure to the active energy radiation. However, either a part or whole of the compound (X) is left unreacted within a normal operation time to combine adherends. This allows the adhesive composition to develop cohesion commensurate with the properties and conversion of the compound (X) and reach a sufficient adhesive level to provide temporary fixing, making it suitable for use in adhesively joining various adherends.

Even after exposure to the active energy radiation, a crosslinking or polymerization reaction is still allowed to proceed in the form of a dark reaction. This is accompanied by rapid reduction in residual content of the compound (X) and thus rapid cure of the composition.

It is preferred that a conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation is in the range of 10 - 70 % and the adhesive composition immediately after its exposure to the active energy radiation exhibits a dynamic tensile modulus in the range of $10^5 - 10^7$ Pa. Accordingly, the highly elastic cured composition is obtained when the substantial absence of the compound (X) is established after exposure of the composition to the active energy radiation.

It is also preferred that the compound (X) immediately

after exposure of the adhesive composition to the active energy radiation exhibits a conversion of not exceeding 30 %, the composition has a viscosity at 25 °C in the range of 1 - 10,000,000 cps, and the compound (X) after exposure of the adhesive composition to the active energy radiation and following 12-hour aging thereof at 25 °C exhibits a conversion in the range of 50 - 100 %. In this case, the flowability is sustained over a certain time after exposure of the composition to the active energy radiation. This accordingly results in the provision of the adhesive composition excellent in wettability with respect to rough surfaces. This adhesive composition is thus made suitable for use in adhesively joining adherends such as mortar and plywood.

The dynamic shear modulus and dynamic tensile modulus, as defined in this specification, were determined by using a viscoelastic spectrometer at a measurement temperature of 25 °C. The dynamic shear modulus values were determined at an applied frequency of 0.1 rad/s. The dynamic tensile modulus values were determined at an applied frequency of 63 rad/s. A tensile tester with a crosshead speed of 500 mm/min was utilized to determine values for elongation at break at a temperature of 25 °C according to JIS K 6301.

Besides the aforementioned compounds (X) and (Y), the adhesive composition in accordance with this invention may

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further contain other components. An adhesive composition in accordance with the below-described second invention is such an adhesive composition that contains the compound (X), the compound (Y) and additional components.

5 The adhesive composition in accordance with the second invention contains: (A) a compound having at least two hydrolyzable silyl groups in a molecule, (B) a compound which induces crosslinking of the compound (A), (C) a compound having a polymerizable group in a molecule, (D) a
10 compound which, when exposed to a radiation, initiates polymerization of the polymerizable group in the compound (C), and (E) a thixotropic agent. That is, the compound (A) and the compound (C) for use in the second invention, in combination, correspond to the compound (X) for use in the
15 first invention, and the compound (D) does to the compound (Y) for use in the first invention. The compound (B) is a catalyst that promotes crosslinking of the compound (A) in the presence of moisture.

20 If stated differently, in addition to containing the adhesive composition in accordance with the first invention, the adhesive composition in accordance with the second invention further contains the compound (B) serving as a catalyst to promote crosslinking of the compound (A), and the thixotropic agent (E).

25 In the adhesive composition in accordance with the

second invention, it is preferred that the hydrolyzable
silyl group in the compound (A) is an alkoxysilyl group and
the compound (A) is a compound containing the alkoxysilyl
group substituted in a polymer selected from polyalkylene
glycol and polyolefin.

In the adhesive composition in accordance with the
second invention, it is preferred that the polymerizable
group in the compound (C) is a free-radically polymerizable
group and the compound (D) is a photochemically free-radical
generating agent. In a more limited aspect of the second
invention, the polymerizable group in the compound (C) is an
acryloyl or methacryloyl group.

In a further limited aspect of the second invention,
the compound (C) includes at least one type of polymerizable
compound (F) containing one or more polymerizable groups in
a molecule and having a weight average molecular weight of
not less than 3,000. The use of the compound (F) for a part
of the compound (F) increases an initial creep resistance of
the adhesive composition immediately after combination of
adherends.

In another particular aspect of the adhesive
composition in accordance with the second invention, the
thixotropic agent (E) is at least one selected from the
group consisting of glass balloons, glass beads, surface-
treated calcium carbonates and silicas.

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The method of joining members in accordance with the present invention is characterized as comprising, in sequence, applying the adhesive composition of the first or second invention to one of the members, exposing a top
5 surface of the applied adhesive composition layer to an active energy radiation and combining the one member with the other member.

The present invention is now described in detail.

(First Invention)

10 In the first invention, the type of the crosslinkable or polymerizable group incorporated in the compound (X) is not particularly specified. Examples of such groups include hydrolyzable silyl groups such as alkoxysilyl, acetoxysilyl, chlorosilyl and bromosilyl groups; oxirane groups such as
15 epoxy and oxetanyl groups; isocyanate groups; polymerizable unsaturated groups such as acryloyl, methacryloyl, styryl, allyl, vinyloxy, vinyloxycarbonyl, maleimide and unsaturated acid anhydride groups; and the like. The compound (X) may contain one or more of the above-listed groups in a molecule
20 and such compounds may be used in combination.

Specific examples of compounds (X) include below-listed compounds (A), compounds (C) and compounds containing one or more isocyanate groups in a molecule. Examples of aromatic monofunctional isocyanates include phenyl isocyanate,
25 naphthyl isocyanate, 2,4-dimethoxydiphenyl isocyanate, 2,6-

dimethylphenyl isocyanate, 3,5-dimethylphenyl isocyanate, 3-acetophenyl isocyanate, 2-biphenyl isocyanate, 2,6-di-isopropylphenyl isocyanate, 2-ethoxyphenyl isocyanate, 4-ethoxyphenyl isocyanate, 2-ethylphenyl isocyanate, 4-heptyl-
5 oxy-phenyl isocyanate, 4-isopropylphenyl isocyanate, 2-methoxyphenyl isocyanate, 3-methoxyphenyl isocyanate, 4-methoxyphenyl isocyanate, 4-methyl-3-nitrophenyl isocyanate, 2-nitrophenyl isocyanate, 3-nitrophenyl isocyanate, 4-nitrophenyl isocyanate, 2-phenoxyphenyl isocyanate, 2-propyl-
10 phenyl isocyanate, o-tolyl isocyanate, m-tolyl isocyanate and p-tolyl isocyanate.

Examples of aliphatic monofunctional isocyanates include cyclohexyl isocyanate, pentyl isocyanate, octyl isocyanate, benzyl isocyanate, dodecyl isocyanate, ethyl
15 isocyanate, heptyl isocyanate, ethoxycarbonyl isocyanate, hexadecyl isocyanate, hexyl isocyanate, 4-methoxybenzyl isocyanate, 2-methylbenzyl isocyanate, 3-methylbenzyl isocyanate and 4-methylbenzyl isocyanate.

Examples of aromatic diisocyanates include 2,4-tolylene
20 diisocyanate (TDI), phenyl diisocyanate, xylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), a mixture (crude MDI) of MDI with triphenylmethane triisocyanate or the like, 1,5-naphthylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, ethylene diisocya-
25 nate, methylene diisocyanate, propylene diisocyanate, tetra-

methylene diisocyanate and tolidine diisocyanate.

Examples of aliphatic diisocyanates include hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), xylylene diisocyanate, hydrogenated xylylene diisocyanate and dicyclohexylpentane diisocyanate.

Examples of tri- and higher-functional polyisocyanates include triphenylmethane triisocyanate, polymethylene polyphenyl polyisocyanate, TMP-modified TDI, an isocyanurate of TDI, TMP-modified HDI, an isocyanurate of HDI, a biuret of HDI, TMP-modified IPDI and an isocyanurate of IPDI.

The above-listed isocyanate compounds may be used alone or in combination.

The compound (Y) may be suitably chosen depending upon the type of the compound (X) used. Examples of compounds (Y) include those which generate, via photodegradation, active species reactive with the polymerizable group in the compound (X), such as photochemically radical-generating, cation-generating, acid-generating and amine generating agents which are below listed as examples of compounds (D).

Such compounds (Y) may be used in combination.

Examples of photochemically amine-generating agents which generate amine upon exposure to a radiation include acyloxy-imino-containing compounds, carbamoyloxyimino-containing compounds and o-nitrobenzyl carbamate.

Particularly preferred are carbamoyloxyimino-containing

compounds represented by the following structural formula:

R1: n-valent organic group;

R2: organic group such as an aromatic or alkyl group;

5 R3: organic group such as an aromatic or alkyl group;

n: integer of 1 or higher; and

preferred combination of R2 and R3, (R2, R3) = (methyl, phenyl) or (methyl, naphthyl)

10 The compounds defined by the above structural formula can be obtained via a reaction of an urethane polymer or an isocyanate compound with an oxime compound. Any technique known in the art can be utilized to effect such a reaction. For example, the defined compounds can be obtained by charging the reactants such that equimolar amounts of
15 isocyanate moieties and hydroxyl moieties in oxime are introduced, optionally adding reaction catalysts such as tin and tertiary amine catalysts for isocyanate and hydroxyl groups, and allowing the reactant to react.

20 If necessary, various additives can be added including a property control agent which will be later described, extender, reinforcer, plasticiser, coloring agent, flame retardant, antisagging agent, antioxidant, age resister, UV absorber, solvent, perfume, pigment, dye, sensitizer for the compound (Y) and the like.

25 The active energy radiation may for example be in the

form of ultraviolet radiation, visible light, infrared ray, electron beam or X-ray.

A source of active energy radiation is suitably chosen depending upon its form of radiation. Suitable sources of active energy radiation include ultrahigh-pressure mercury lamps, high-pressure mercury lamps, medium-pressure mercury lamps, low-pressure mercury lamps, metal halide lamps, black light lamps, microwave-activated mercury lamps, halogen lamps, excimer laser, xenon lamps, fluorescent lamps, sunlight, electron beam emitter and the like.

In the first invention, a conversion of the compound (X) is defined by the following equation:

$$\text{Conversion (\%)} = [a(0) - a(t)/a(0)] \times 100$$

where,

$a(0)$ = content of the compound (X) in an adhesive composition prior to being exposed to an active energy radiation; and

$a(t)$ = content of the compound (X) in an adhesive composition when t hours lapsed after exposure to an active energy radiation.

The amount of the compound (X) incorporated in the composition can be determined by a method as appropriate to the compound (X) used. Examples of such determination methods include gel permeation chromatography, thin-layer chromatography, affinity chromatography, normal phase

chromatography, reversed phase chromatography, infrared spectroscopy, nuclear magnetic resonance spectroscopy, titration as appropriate to the crosslinkable or polymerizable group, quantitative determination by gel fraction and the like.

Also in the first invention, the adhesive composition prior to exposure to the active energy radiation exhibits a viscosity in the range of 1 - 10,000,000 cps at 25 °C. If over 10,000,000 cps, the viscosity is too high to result in satisfactory application of the composition to an adherend. The viscosity in this specification is expressed by a value determined using a Brookfield viscometer with a rotor rotation speed of 10 rpm.

Immediately after exposure of the adhesive composition in accordance with the first invention to the active energy radiation, the compound (X) shows a conversion in the range of 0 - 70 %. That is, when the composition is exposed to the active energy radiation, the compound (Y) is caused to decompose rapidly. On the other hand, the crosslinkable or polymerizable compound (X) is, either in part or whole, left unreacted within a time of a normal combining operation. Accordingly, the composition develops cohesion commensurate with the properties and residual content of the compound (X) to show a sufficient level of adhesion to provide temporary fixing, or alternatively, completes crosslinking rapidly

while maintaining sufficient flowability to remain wettable. These permit easy and reliable adhesion of the composition to adherends.

After exposure of the adhesive composition to the active energy radiation and following 24-hour aging thereof at 25 °C, the compound (X) exhibits a conversion in the range of 50 - 100 % and the cured composition shows an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of 10^5 - 10^9 Pa. Accordingly, the composition after cure has improved impact-resistant and durable adhesive properties.

That is, even after exposure to the active energy radiation, a crosslinking or polymerization reaction is still allowed to proceed in the form of a dark reaction. This is accompanied by rapid reduction in residual content of the compound (X), resulting in the provision of a cured product with improved impact-resistant and durable adhesive properties.

(Second Invention)

In the second invention, the compound (A) is used having two or more hydrolyzable silyl groups in a molecule. The hydrolyzable silyl group is not particularly specified in type. Examples of hydrolyzable silyl groups include those derived via replacement of at least one hydrogen atom of a silyl group by an alkoxy, oxime, alkenyl-oxy, acetox

or halogen group. The use of the hydrolyzable silyl group (alkoxysilyl group) derived via replacement of at least one hydrogen atom by an alkoxy group is preferred for its superior storage stability.

5 Preferably, a polymer having at least two hydrolyzable silyl groups in a molecule is used for the aforementioned hydrolyzable silyl-containing or alkoxysilyl-containing compound. The use of such a polymer eases viscosity design of the adhesive composition and imparts the well-balanced
10 cohesion and adhesion to the adhesive composition after cure. The polymer is not particularly specified in type. Examples of useful polymers include propylene glycol, ethylene glycol and other polyalkylene glycols, polyester, polyamide, polycarbonate, polymethacrylate, polyacrylate,
15 polystyrene, polyolefin, copolymers thereof and the like. Preferred among the above-listed polymers are polyalkylene glycol and polyolefin. These polymers preferably have a weight average molecular weight of 4,000 - 30,000. More preferably, they have a weight average molecular weight of
20 10,000 - 30,000 and a molecular weight distribution (M_w/M_n) of 1.6 or below.

The alkoxysilyl group, as used herein, encompasses a monoalkylsilyl group, a dialkoxysilyl group and a trialkoxy-
25 silyl group. Examples of alkoxy groups include methoxy, ethoxy, propyloxy, isopropyloxy, butoxy, tert-butoxy,

phenoxy, benzyloxy groups. In the case of dialkoxysilyl and trialkoxy-silyl groups, the above-listed alkoxy groups may be used alone or in combination.

The substituting alkoxysilyl group may be placed either at an end or on a side chain of the polymer. It may be placed at both locations.

Also, examples of useful compounds (A) are commercially available, including Kaneka MS Polymers such as MS Polymer S-203, 303 and 903, Kaneka Silyl Polymers such as Silyl SAT-200, MA-403 and MA-447, and Asahi Glass ExceStar ESS-2410, 2420 and 3630.

The type of the compound (B) used to induce crosslinking of the compound (A) is not particularly specified, so long as it shows an accelerating or catalytic action when the crosslinking of the compound (A) is caused to occur in the presence of moisture in the air. Examples include tin compounds such as dibutyltin dilaurate, dibutyltin oxide, dibutyltin diacetate, dibutyltin phthalate, bis(dibutyltin laurate) oxide, dibutyltin bis-acetylacetonate, dibutyltin bis(monoester malate), tin octylate, dibutyltin octoate and dioctyltin oxide; titanate compounds such as tetra-n-butoxy titanate and tetraisopropoxy titanate; amine salts such as dibutylamine-2-ethyl hexoate; and other acid catalysts and basic catalysts. These compounds may be used alone or in

combination.

The type of the compound (C) having a polymerizable group in a molecule is not particularly specified, so long as it has a polymerizable substituting group in such as a free-radically polymerizable or cationically polymerizable group. It may contain two or more dissimilar polymerizable groups in a molecule.

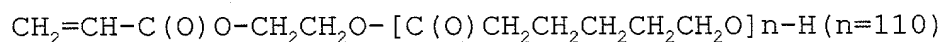
Examples of free-radically polymerizable groups include styryl, acryloyl, methacryloyl, vinyl ester groups and the like. Acryloyl and methacryloyl groups are preferred for their superior polymerizability.

Examples of styryl-containing compounds include styrene, indene, α -methylstyrene, p-methylstyrene, p-chlorostyrene, p-chloromethylstyrene, p-methoxystyrene, p-tert-butoxystyrene, divinylbenzene and the like.

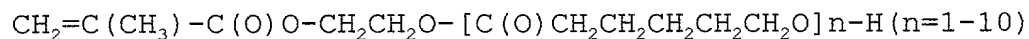
Examples of acryloyl-containing or methacryloyl-containing compounds include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, isomyristyl (meth)acrylate, stearyl (meth)acrylate, isobornyl (meth)acrylate, benzyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, glycidyl (meth)acrylate, tetrahydrofurfuryl

(meth)acrylate, hexanediol di(meth)acrylate, ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, epoxy acrylate, polyester acrylate, urethane acrylate, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 5-hydroxypentyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 3-hydroxy-3-methylbutyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, pentaerythritol tri(meth)acrylate, 2-[(meth)acryloyloxy]ethyl 2-hydroxyethyl phthalate, 2-[(meth)acryloyloxy]ethyl 2-hydroxypropyl phthalate and the following compounds:

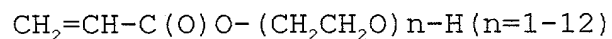
Compound 1



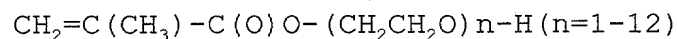
Compound 2



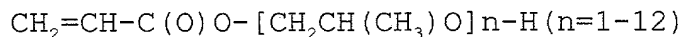
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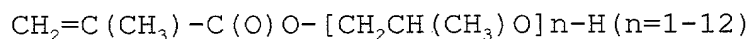
Compound 4



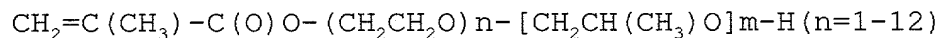
Compound 5



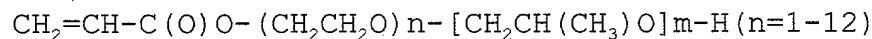
Compound 6



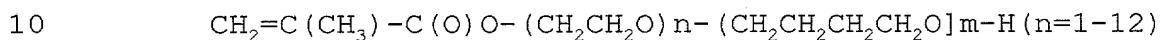
5 Compound 7



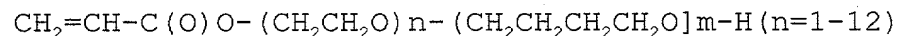
Compound 8



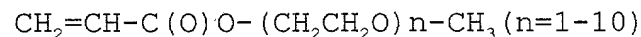
Compound 9



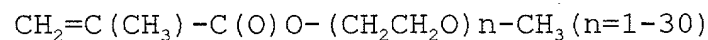
Compound 10



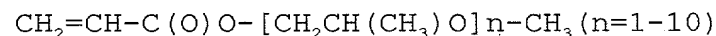
Compound 11



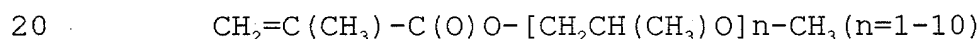
15 Compound 12



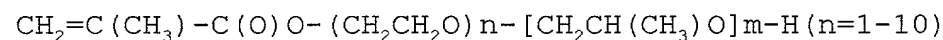
Compound 13



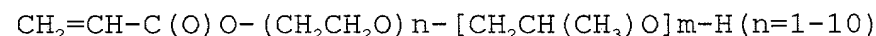
Compound 14



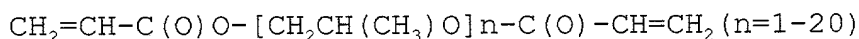
Compound 15



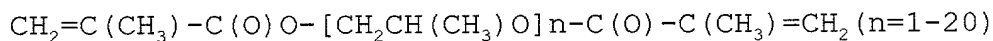
Compound 16



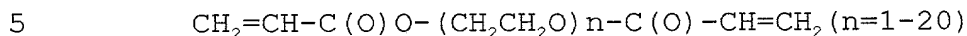
25 Compound 17



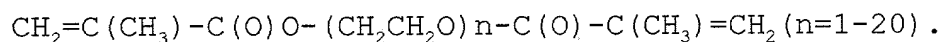
Compound 18



Compound 19



Compound 20



Examples of vinyl ester-containing compounds include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl caproate, vinyl benzoate and vinyl cinnamate.

Examples of cationically polymerizable groups include epoxy, oxetanyl, vinyloxy and styryl groups.

Examples of epoxy-containing compounds include bisphenol A epoxy resins, hydrogenated bisphenol A epoxy resins, bisphenol F epoxy resins, novolac epoxy resins, cycloaliphatic epoxy resins, brominated epoxy resins, rubber modified epoxy resins, urethane modified epoxy resins, glycidyl ester compounds, epoxidized polybutadiene and epoxidized styrene-butadiene-styrene copolymers.

20 Examples of oxetanyl-containing compounds include 3-ethyl-3-hydroxymethyloxetane, 3-ethyl-3-phenoxyethyl-oxetane, 3-ethyl-3-hexyloxymethyloxetane, 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene and the like.

25 Examples of vinyloxy-containing compounds include n-propyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl

ether, tert-butyl vinyl ether, tert-amyl vinyl ether,
cyclohexyl vinyl ether, 2-ethylhexyl vinyl ether, dodecyl
vinyl ether, octadecyl vinyl ether, 2-chloroethyl vinyl
ether, ethylene glycol butyl vinyl ether, triethylene glycol
5 methyl vinyl ether, (4-vinyloxy)butyl benzoate, ethylene
glycol divinyl ether, diethylene glycol divinyl ether,
triethylene glycol divinyl ether, tetraethylene glycol
divinyl ether, butane-1,4-diol-divinyl ether, hexane-1,6-
diol-divinyl ether, cyclohexane-1,4-dimethanol-divinyl
10 ether, di(4-vinyloxy)butyl isophthalate, di(4-vinyloxy)butyl
glutarate, di(4-vinyloxy)butyl succinate, trimethylolpropane
trivinyl ether, 2-hydroxyethyl vinyl ether, 4-hydroxybutyl
vinyl ether, 6-hydroxyhexyl vinyl ether, cyclohexane-1,4-
dimethanol-monovinyl ether, diethylene glycol monovinyl
15 ether, 3-aminopropyl vinyl ether, 2-(N,N-diethylamino)ethyl
vinyl ether, urethane vinyl ether, polyester vinyl ether and
the like.

Examples of styryl-containing compounds include
styrene, indene, α -methylstyrene, p-methylstyrene, p-
20 chlorostyrene, p-chloromethylstyrene, p-methoxystyrene, p-
tert-butoxystyrene, divinylbenzene and the like.

Preferably, the compound (F) is used for a part of the
compound (C). The compound (F) is a polymerizable compound
containing at least one polymerizable group in a molecule
25 and having a weight average molecular weight of 3,000 or

greater. The type of this polymerizable compound (F) is not particularly specified if it gives a long distance between crosslinks, develops cohesion, contains at least one free-radically polymerizable group and has a molecular weight of 3,000 or greater. Examples of compounds (F) include polymerizable compounds derived via terminal modification of polystyrene, polymethyl methacrylate, polypropylene or polyethylene butylene; urethane acrylate; polyether acrylate and the like.

The use of the compound (F) for a part of the compound (C) increases a creep resistance of the adhesive composition initially after combination of adherends.

Preferably, the weight of the compound (F) in 100 parts compound (C) is 0.1 - 70 parts. If the weight of the compound (F) is below 0.1 parts, the effectiveness of using the compound (F) may become negligible. On the other hand, if it exceeds 70 parts, irradiation may in some cases cause a marked increase in cohesion and accordingly a decrease in wettability of the adhesive composition to adherends, which results in the failure to obtain the sufficient creep resistance.

The compound (D) that photoinitiates polymerization of the polymerizable group in the compound (C) can be suitably chosen depending upon the polymerization reaction mechanism of the polymerizable group contained in the compound (C).

radiation. Examples of such compounds include iron-allene complex compounds, aromatic diazonium salts, aromatic iodonium salts, aromatic sulfonium salts, pyridinium, aluminum complex/silanol salts and the like. These are also commercially available, examples of which include Ciba Geigy IRGACURE 261, Asahi Denka OPTOMER SP-150, SP-151, SP-170 and SP-171, General Electric UVE-1014, Sartomer CD-1012, Sanshin Chemical SANAID SI-60L, SI-80L and SI-100L, Nippon Soda CI-2064, CI-2639, CI-2624 and CI-2481, Rhone Poulenc RHODORSIL PHOTOINITIATOR 2074, Union Carbide UVI-6990, Midori Chemical BBI-103, MPI-103, TPS-103, MDS-103, DTS-103, NAT-103 and NDS-103, and the like. In the approximate temperature range of 20 - 80 °C, the use of compounds having low thermal catalytic activities is preferred in terms of storage stability. The above-listed compounds may be used alone or in combination.

When desired, a photosensitizer may also be added to increase a radiation sensitivity of the photochemically cation-generating agent. Suitable photosensitizers include anthracene, perylene, coronene, tetracene, benzanthracene, phenothiazine, flavin, acridine, ketocoumarin, thioxanthone derivatives, benzophenone, acetophenone, 2-chloro-thioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, isopropylthioxanthone and the like.

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The wavelength photosensitivity of the compound (D) is not particularly specified, but the use of the compound which is sensitive to a radiation in the wavelength region of 300 - 800 nm is preferred. The compound (D), if only
5 sensitive in the wavelength region below 300 nm, is able to obtain a sufficient energy to initiate rapid polymerization or crosslinking of the compound (C), but thick coating of the adhesive composition containing such a compound may lead to an increase in cohesion of its surface alone, possibly
10 resulting in the uneven development of initial cohesion over its entire bulk or in the marked decrease in wettability of its irradiated surface. On the other hand, the compound (D), if only sensitive in the wavelength region over 800 nm, tends to readily decompose even at a low energy (thermal
15 energy) level and initiate polymerization or crosslinking of the compound (C). This tendency may in some cases adversely affect the storage stability.

The thixotropic agent (E) may be suitably chosen from compounds which can impart a thixotropic property to the
20 adhesive composition. Examples of such compounds include various silicas such as colloidal silica, surface-treated calcium carbonates such as hydrophobic calcium carbonate, glass balloons, glass beads, polyvinyl pyrrolidone and the like. Among these, glass balloons, glass beads, various
25 silicas and surface-treated calcium carbonates are

preferred. Preferably, this thixotropic agent has a surface with a high affinity for the compound (A) or (C) for use in the adhesive composition of the present invention. Where urethane acrylate is used for the compound (C), the

5 thixotropic agent (E) is preferably in the form of glass balloons. Where α,ω -diacryloyl-poly(propylene glycol) is used for the compound (C), the use of surface-treated substances, e.g., surface-treated calcium carbonates, is preferred.

10 The blending proportions of the components incorporated in the adhesive composition of the second invention are not particularly specified, so long as they enable the adhesive composition to exhibit the superior application properties with a machine and improved storage stability, extended pot

15 life, and the ability to develop initial cohesion by short-time irradiation. Illustrating the preferred blending proportions, 0.01 - 20 parts by weight of the compound (B) which initiates crosslinking of the compound (A), 15 - 100 parts by weight of the compound (C) having a polymerizable

20 group in a molecule, and 0.01 - 20 parts by weight of the compound (D) which initiates polymerization of the polymerizable group in the compound (C) upon exposure to a radiation are incorporated, based on 100 parts by weight of the compound (A) having at least two hydrolyzable silyl

25 groups in a molecule. Preferably, the thixotropic agent (E)

is added in the amount of 20 - 65 % by volume (25 °C), based on 100 % by volume of all compounds (A) - (E).

If the amount of the compound (B) incorporated in the composition is below 0.01 parts by weight, a cure rate of the compound (A) may in some cases be reduced to the degree that is substantially unsuited for a practical use. By contrast, the amount of exceeding 20 parts by weight, while effective to accelerate the cure rate sufficiently, affects markedly on a bulk after cure to sometimes result in the difficulty to obtain sufficient adhesive strength.

If the amount of the compound (C) incorporated in the composition is below 15 parts by weight, the expected initial cohesion may not result from photopolymerization or photocrosslinking, even with the addition of excess amount of the thixotropic agent. On the other hand, the amount of exceeding 100 parts by weight, while effective to impart the sufficient initial cohesion after cure, sometimes increases the cohesion excessively to reduce wettability of the adhesive composition, resulting in the failure to exhibit sufficient initial adhesiveness.

If the amount of the compound (D) incorporated in the composition is below 0.01 parts by weight, a polymerization or crosslinking rate of the compound (C) by irradiation may be reduced by a marked extent, resulting in the failure for the adhesive composition to exhibit initial adhesion after

exposure to a radiation. On the other hand, the amount of exceeding 20 parts by weight, while effective to accelerate a cure rate sufficiently, affects markedly on a bulk after cure to sometimes result in the difficulty to obtain sufficient adhesive strength.

If the amount of the thixotropic agent (E) incorporated in the composition is below 20 % by volume, it may become difficult to obtain a sufficient thixotropic property. The difficulty to obtain initial adhesion after exposure to a radiation may also result. By contrast, if it exceeds 65 % by volume, the adhesive composition of the present invention may show a marked viscosity increase, resulting in the difficult application thereof by a machine or in the marked reduction of the application rate.

Various additives can be added, when needed, to the adhesive composition of the present invention. Examples of additives include property control agents such as for improving tensile properties, extenders, reinforcers, plasticizers, colorants, flame retarders and the like.

Illustrative of property control agents such as for improving tensile properties are various silane coupling agents, including vinyltrimethoxysilane, dimethyldimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, tetramethoxysilane, tetraethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, 3-aminopropyltrimethoxy-

silane, 3-aminopropylmethyldimethoxysilane, 3-aminopropyl-
triethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxy-
silane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N,N'-
bis-[3-(trimethoxysilyl)propyl]ethylenediamine, N,N'-bis-[3-
5 (triethoxysilyl)propyl]ethylenediamine, N,N'-bis-[3-
(trimethoxysilyl)propyl]hexaethylenediamine, N,N'-bis-[3-
(triethoxysilyl)propyl]hexaethylenediamine and the like.
These may be used alone or in combination.

Suitable for use as extenders are those which, when
10 added to the adhesive composition in accordance with the
present invention, do not provide significant effect on the
thixotropic properties thereof. Examples of extenders
include talc, clay, calcium carbonate, magnesium carbonate,
anhydrous silicon, hydrated silicon, calcium silicate,
15 titanium dioxide, carbon black and the like. These may be
used alone or in combination.

Examples of plasticizers include phosphate esters such
as tributyl phosphate and tricresyl phosphate, phthalate
esters such as dioctyl phthalate, aliphatic esters of mono-
20 basic acid such as glycerol monooleate ester, aliphatic
esters of dibasic acid such as dioctyl adipate, poly-
propylene glycols and the like. These may be used alone or
in combination.

Other than the above-described additives, the adhesive
25 composition of the present invention may also contain an

antisagging agent, antioxidant, age resister, UV absorber, solvent, perfume, pigment, dye or the like, when necessary.

The method of joining members in accordance with the present invention is characterized as comprising, in
5 sequence, applying the adhesive composition of the first or second invention to one member, exposing a top surface of the applied adhesive composition layer to a radiation and combining the one member with the other member.

In the joining method, in the case where both members
10 permit substantially no transmission of a radiation, it becomes difficult to expose the adhesive composition to a radiation after application of the adhesive composition to one member and subsequent combination thereof with the other member. On the other hand, even if one attempted to apply
15 the irradiated adhesive composition to one member and then combine the one member with other member, the difficulty to apply the adhesive composition still remains, since the adhesive composition increases its viscosity and shows a marked cohesion increase upon exposure to a radiation.

In the joining method of the present invention, the
20 radiation source is not particularly specified, so long as it can emit a radiation including a wavelength region that corresponds to an absorption region of the compound (C) or the sensitizer added to improve photo-sensitivity, and is
25 suitably chosen depending upon the type of the compound (C)

or the sensitizer used. Examples of suitable radiation sources include low-pressure mercury lamps, medium-pressure mercury lamps, high-pressure mercury lamps, ultrahigh-pressure mercury lamps, excimer laser, chemical lamps, black light lamps, microwave-activated mercury lamps, metal halide lamps, sodium lamps, fluorescent lamps, sunlight and the like.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is described in more detail with reference to the following non-limiting examples.

(1) Preparation of Adhesive Compositions

(EXAMPLES 1 - 13 AND COMPARATIVE EXAMPLES 1 - 5)

According to the formulations shown in Tables 1 - 3, the compounds (A), (B), (C) and (D), optionally with the compound (F), were first mixed with stirring to homogeneity in a beaker protected against a radiation by an aluminum foil (the blend, if containing a powder, was mixed under a light-shielded condition while maintained at 50 °C). After the blend was mixed to homogeneity, the thixotropic agent (E) was added and dispersed therein using a stirring machine (TK HOMO DISPER manufactured by Tokushu Kika Kogyo Co., Ltd.) under a stirring condition of 500 rpm x 10 minutes. As a result, adhesive compositions of the present invention were obtained.

(EXAMPLE 14)

(Synthesis of Urethane Prepolymer)

100 parts by weight of polyethertriol (ADEKA Polyether
T-4000, product of Asahi Denka Industries) derived from
5 trimethylolpropane having a molecular weight of 4,000 and
propylene oxide, 100 parts by weight of propylene oxide
(molecular weight of 6,000) and hexamethylene diisocyanate
were mixed such that a ratio NCO/OH was brought to 1.9. The
mixture was allowed to react at 80 °C for 5 hours. As a
10 result, a urethane prepolymer was obtained.

(Synthesis of Photochemically Amine-Generating Agent)

0.1 mole acetophenoneoxime dissolved in 100 ml THF was
added to 0.05 mole hexamethylene diisocyanate. The mixture
was stirred under dry and nitrogen atmosphere at 50 °C for 4
15 hours. Thereafter, THF was allowed to volatilize. The
resulting white solid was dissolved in MEK at 80 °C and
recrystallized therefrom to achieve purification. The
purified compound was rendered as a photochemically amine-
generating agent.

20 (Preparation of Composition)

The photochemically amine-generating agent and
anthracene photosensitizer were added to 100 parts by weight
of the above-obtained urethane prepolymer in the respective
amounts specified in Table 4. The mixture was stirred to
25 homogeneity to obtain a composition.

(COMPARATIVE EXAMPLE 6)

The urethane prepolymer obtained in Example 14 was used alone to prepare a composition of Comparative Example 6.

(2) PERFORMANCE EVALUATION METHODS

5 The adhesive compositions obtained in Examples 1 - 14 and Comparative Examples 1 - 6 were evaluated for viscosity, compressive shear bond strength, shear creep, pot life (working life), initial creep resistance, conversion, elongation at break of cured compositions, dynamic tensile modulus and dynamic shear modulus according to the following
10 procedures. The results of Examples 1 - 13 are listed in Tables 5 and 6. The results of Comparative Examples 1 - 5 are listed in Table 7. The results of Example 14 and Comparative Examples 6 are listed in Table 4.

15 1) Viscosity

 The viscosity of the compositions was measured at 25 °C using a rotational viscometer (Brookfield viscometer made by Tokyo Keiki Co., Ltd.) with a number 4 spindle at a rotational speed of 10 rpm, according to JIS K 6833. The
20 spindle number and rotational speed were suitably selected in evaluating the adhesive composition if it excluded the thixotropic agent (E), fell beyond a measurable range under the above conditions or was a Newtonian viscous fluid.

 2) Compressive Shear Bond Strength

25 Each adhesive composition was coated onto a slate

adherend (35 mm x 25 mm x 8 mm). The coated area was 25 mm x 25 mm x 0.3 mm. This slate adherend was combined with another slate adherend to fabricate an evaluation test sample. The sample obtained was subjected to a compressive test (at a crosshead speed of 300 mm/min) according to JIS K 6852, so that the compressive shear bond strength of the composition prior to exposure to a radiation was evaluated.

Next, each adhesive composition was coated on a slate adherend in the same manner as stated above. The coated surface was exposed to an ultraviolet radiation at 365 nm and at an energy of 700 mJ/cm² (Examples 1 - 13 and Comparative Examples 1 - 5) or at an energy of 7,000 mJ/cm² (Example 14 and Comparative Example 6) using a high-pressure mercury lamp. Thereafter, another slate adherend was combined therewith to fabricate an evaluation test sample. The sample obtained was subjected to a compressive test (at a crosshead speed of 300 mm/min) according to JIS K 6852, so that the compressive shear bond strength of the composition after exposure to a radiation was evaluated.

Further, evaluation test samples were fabricated in the same manner as used in evaluating the compressive shear bond strength of the composition immediately after exposure to a radiation. The samples obtained were aged at 25 °C and 63 % humidity for 24 hours, or separately aged for 7 days, and subjected to a compressive test (at a crosshead speed of 300

mm/min) according to JIS K 6852, so that the compressive shear bond strength of the composition either after 24 hours or 7 days from exposure to a radiation was evaluated.

3) Shear Creep (Initial Shear Creep Test)

5 In the fabrication of an evaluation sample, each composition was coated on a pentite steel plate (25 mm x 150 mm x 1 mm). The coated area was 25 mm x 25 mm. The coated composition was exposed to an ultraviolet radiation. After combination with another pentite steel plate (25 mm x 150 mm x 1 mm), the composition was subjected to aging at 23 °C for 10 a duration specified in each Example to obtain an evaluation sample. Creep characteristics were evaluated by suspending one of the adherends of the obtained sample so that the own weight of the other adherend acted as a shear load.

15 Evaluation was made by observing whether or not the load fell within 30 minute from the start of suspension.

4) Pot Life (Working Life)

Each adhesive composition was coated on a glass substrate to a thickness of 0.35 mm and left to stand under 20 conditions of 23 °C and 65 % humidity while maintained unexposed to a radiation. The period of time during which the adhesive composition remained unwebbed after it had been coated on the substrate was evaluated as a pot life.

25 5) Initial Creep Resistance (Initial 90° Peel Creep Test)

Each adhesive composition was coated on a 25 mm x 100 mm x 0.5 mm zinc steel plate to a size of 25 mm x 50 mm x 0.35 mm. The coated surface was exposed to an ultraviolet radiation at 365 nm and at an energy of 700 mJ/cm² (Examples 1 - 13 and Comparative Examples 1 - 5) or at an energy of 7,000 mJ/cm² (Example 14 and Comparative Example 6) using a high-pressure mercury lamp, followed by combination thereof with a 50 mm x 150 mm x 8 mm slate adherend. Immediately after the combination, the slate adherend was fixed at its both ends such that it oriented horizontally and the zinc steel plate faced downward, and a mass of a specific weight was suspended from one end of the zinc steel plate. The maximum weight of the mass which caused no delamination within one hour was recorded. The heavier weight of the mass indicates the increased initial creep resistance.

6) Conversion

Immediately after termination of exposure to an active energy radiation, the adhesive composition was aged at 25 °C for 12 hours or 24 hours. A conversion of the compound (C) in the composition after the 12-hour or 24-hour aging was measured.

In the conversion measurement, the content of the compound (C) in the composition was determined by a gel permeation chromatograph equipped with an RI (Refractive Index) device. The conversion of the compound (C) was

calculated from the ratio of its content in the composition after to before exposure to the active energy radiation.

7) Elongation at Break of Cured Composition

Each composition was exposed to an active energy radiation and subsequently subjected to 24-hour aging at 25 °C. The elongation at break of the cured composition was then measured at 25 °C using a tensile tester at a crosshead speed of 500 mm/minute, according to JIS K 6301.

8) Dynamic Tensile Modulus

Each composition was exposed to an active energy radiation and subsequently subjected to 24-hour aging at 25 °C. The dynamic tensile modulus of the cured composition was then measured at 25 °C using a viscoelastic spectrometer at an applied frequency of 10 Hz.

9) Dynamic Shear Modulus

Each composition was exposed to an active energy radiation. Immediately thereafter, the dynamic shear modulus of the cured composition was measured at 25 °C using a viscoelastic spectrometer at an applied frequency of 0.016 Hz.

[Table 1]

Classification	Composition, Product Name	Maker	Example						
			1	2	3	4	5	6	7
Compound (A)	MS Polymer, S-303	Kaneka Corp.	100	100	100	100	100	100	100
Compound (B)	Tin Catalyst, SB-65	Sankyo Yuki-Gosei Co.	1	1	1	1	1	1	1
Compound (C)	Urethane Acrylate, AH-600	Kyoei Chemical Co.	18	15	-	-	18	18	18
	α,ω -Diacyloyl-Polypropylene Glycol, APG-700	Shin-Nakamura Chem. Ind. Co.	-	-	15	-	-	-	-
	Poly (Propylene Glycol) Mono Acrylate, Biscoat #320	Osaka Org. Chem. Co.	-	15	5	-	-	-	-
	3-Phenoxy-2-Hydroxypropyl Acrylate, M-600A	Kyoei Chemical Co.	-	-	-	80	-	-	-
Compound (F)	P-Cumyl Phenol Ethylene Oxide Modified Acrylate, Aronix M-110	Toagosei Co.	-	-	-	-	-	-	-
	Polymethyl Methacrylate Macromonomer, AA-6	Toagosei Co.	-	-	-	-	-	-	-
	Urethane Acrylate, Aronix M-1310	Toagosei Co.	-	-	-	-	-	-	-
Compound (D)	Irgacure-819	Ciba Specialty Chemical Co.	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Thixotropic Agent (E)	Glass Balloon, Q-Cell 520	PQ Australia Pty. Co.	-	-	-	-	60	50	-
	Surface-Treated Calcium Carbonate, Viscolite U	Shiraishi Ind. Co.	-	-	-	-	-	-	30

Units of formulated compositions: Compounds (A)-(D) in parts by weight and Thixotropic agent (E) in % by volume

[Table 2]

			Example						
Classification	Composition, Product Name	Maker	8	9	10	11	12	13	
Compound (A)	MS Polymer, S-303	Kaneka Corp.	100	100	100	100	100	100	
Compound (B)	Tin Catalyst, SB-65	Sankyo Yuki-Gosei Co.	1	1	1	1	1	1	
Compound (C)	Urethane Acrylate, AH-600	Kyoei Chemical Co.	18	15	-	-	15	-	
	α,ω -Diacryloyl-Polypropylene Glycol, APG-700	Shin-Nakamura Chem. Ind. Co.	-	-	15	-	-	-	
	Poly (Propylene Glycol) Mono Acrylate, Biscoat #320	Osaka Org. Chem. Co.	-	15	5	-	15	-	
	3-Phenoxy-2-Hydroxypropyl Acrylate, M-600A	Kyoei Chemical Co.	-	-	-	80	-	-	
Compound (F)	P-Cumyl Phenol Ethylene Oxide Modified Acrylate, Aronix M-110	Toagosei Co.	-	-	-	-	-	30	
	Polymethyl Methacrylate Macromonomer, AA-6	Toagosei Co.	-	-	-	-	1	-	
	Urethane Acrylate, Aronix M-1310	Toagosei Co.	-	-	-	-	-	30	
Compound (D)	Irgacure-819	Ciba Specialty Chemical Co.	0.5	0.5	0.5	0.5	0.5	0.5	
Thixotropic Agent (E)	Glass Balloon, Q-Cell 520	PQ Australia Pty. Co.	-	60	-	-	-	-	
	Surface-Treated Calcium Carbonate, Viscolite U	Shiraishi Ind. Co.	50	-	50	40	60	50	

Units of formulated compositions: Compounds (A)-(D) in parts by weight and Thixotropic agent (E) in % by volume

[Table 3]

Classification	Composition, Product Name	Maker	Comparative Example				
			1	2	3	4	5
Compound (A)	MS Polymer, S-303	Kaneka Corp.	100	100	100	-	100
Compound (B)	Tin Catalyst, SB-65	Sankyo Yuki-Gosei Co.	-	1	1	1	1
Compound (C)	Urethane Acrylate, AH-600	Kyoei Chemical Co.	-	-	-	-	10
	α,ω -Diacyloyl-Polypropylene Glycol, APG-700	Shin-Nakamura Chem. Ind. Co.	-	-	-	100	-
	Poly (Propylene Glycol) Mono Acrylate, Biscoat #320	Osaka Org. Chem. Co.	-	-	-	-	-
	3-Phenoxy-2-Hydroxypropyl Acrylate, M-600A	Kyoei Chemical Co.	-	-	-	-	-
	P-Cumyl Phenol Ethylene Oxide Modified Acrylate, Aronix M-110	Toagosei Co.	-	-	-	-	-
Compound (F)	Polymethyl Methacrylate Macromonomer, AA-6	Toagosei Co.	-	-	-	-	-
	Urethane Acrylate, Aronix M-1310	Toagosei Co.	-	-	-	-	-
Compound (D)	Irgacure-819	Ciba Specialty Chemical Co.	-	-	-	0.5	0.5
Thixotropic Agent (E)	Glass Balloon, Q-Cell 520	PQ Australia Pty. Co.	-	-	60	-	-
	Surface-Treated Calcium Carbonate, Viscolite U	Shiraishi Ind. Co.	-	-	-	-	-

Units of formulated compositions: Compounds (A)-(D) in parts by weight and Thixotropic agent (E) in % by volume

[Table 4]

			Example 14	Comparative Example 6
Formulated Composition	Urethane Prepolymer		100	100
	Photochemical Amine Generating Agent		10	-
	Photosensitizer Anthracene		0.5	-
Performance Evaluation	Viscosity (cps)	Before Irradiation	100000	100000
		Imm. After Irradiation	100000	100000
	Compressive Shear Bond Strength (kgf/cm ²)	Before Irradiation	<0.01	<0.01
		Imm. After Irradiation	<0.01	<0.01
		24 Hrs. After Irradiation	6.5	1.2
		7 Days After Irradiation	7.1	3.1
	Shear Creep	Imm. After Irradiation	Fell	Fell
		5 Min. After Irradiation	Sustained	Fell
	Pot Life (hrs.)		> 12	> 12
	Conversion (%)	Imm. After Irradiation	14	0
		12 Hrs. After Irradiation	55	5
		24 Hrs. After Irradiation	90	32
	Elongation at Break (%)		290	Immeasurable
Dynamic Tensile Modulus (Pa)		1.79 × 10 ⁶	Immeasurable	

[Table 5]

		Example						
		1	2	3	4	5	6	7
Viscosity (cps)		14000	10000	12000	500	440000	330000	250000
Compressive Shear Bond Strength (kgf/cm ²)	Before Irradiation	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Imm. After Irradiation	<0.01	<0.01	<0.01	<0.01	0.4	0.3	0.5
	24 Hrs. After Irradiation	53	65	59	64	14	13	13
7 Days After Irradiation		19	17	16	13	17	16	14
Shear Creep	Imm. After Irradiation	Fell	Fell	Fell.	Sustained	Sustained	Sustained	Sustained
	10 Min. After Irradiation	Sustained	Sustained	Sustained	Sustained	Sustained	Sustained	Sustained
Pot Life (hrs.)		> 12	> 12	> 12	> 12	> 12	> 12	> 12
Initial 90° Peel Creep (g)		<100	<100	<100	<100	200	200	100
Conversion (%)	Imm. After Irradiation	55.3	34	45	51	15	13	55
	12 Hrs. After Irradiation	71	76	64	78	63	57	67
	24 Hrs. After Irradiation	79	81	77	84	72	68	70
Elongation at Break (%)		150	130	110	350	45	75	110
Dynamic Tensile Modulus (Pa)		6.80×10^6	3.90×10^6	5.60×10^5	8.40×10^5	3.05×10^7	1.84×10^7	8.34×10^6
Dynamic Shear Modulus (Pa)		2.59×10^4	2.14×10^4	1.89×10^4	4.33×10^4	8.31×10^5	7.88×10^5	1.19×10^5

[Table 6]

		Example						
		8	9	10	11	12	13	
Viscosity (cps)		450000	400000	340000	6500	400000	480000	
Compressive Shear Bond Strength (kgf/cm ²)	Before Irradiation	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
	Imm. After Irradiation	0.5	0.8	0.5	0.9	0.8	0.6	
	24 Hrs. After Irradiation	10	15	12	14	15	17	
	7 Days After Irradiation	13	16	18	14	16	17	
Shear Creep	Imm. After Irradiation	Sustained	Sustained	Sustained	Sustained	Sustained	Sustained	
	10 Min. After Irradiation	Sustained	Sustained	Sustained	Sustained	Sustained	Sustained	
Pot Life (hrs.)		> 12	> 12	> 12	> 12	> 12	> 12	
Initial 90° Peel Creep (g)		100	200	100	100	400	400	
Conversion (%)	Imm. After Irradiation	59	57	59	39	57	41	
	12 Hrs. After Irradiation	65	68	73	76	80	68	
	24 Hrs. After Irradiation	69	75	82	81	84	73	
Elongation at Break (%)		135	80	130	310	130	145	
Dynamic Tensile Modulus (Pa)		2.11 × 10 ⁷	8.82 × 10 ⁶	4.11 × 10 ⁶	5.37 × 10 ⁶	9.32 × 10 ⁶	1.27 × 10 ⁸	
Dynamic Shear Modulus (Pa)		2.04 × 10 ⁵	9.01 × 10 ⁵	2.00 × 10 ⁵	4.81 × 10 ⁵	8.51 × 10 ⁵	2.89 × 10 ⁵	

[Table 7]

		Comparative Example				
		1	2	3	4	5
Viscosity (cps)		30000	30000	420000	65	35000
Compressive Shear Bond Strength (kgf/cm ²)	Before Irradiation	<0.01	<0.01	<0.01	<0.01	<0.01
	Imm. After Irradiation	<0.01	<0.01	<0.01	*	<0.01
	24 Hrs. After Irradiation	<0.01	0.14	38	*	0.31
7 Days After Irradiation		<0.01	3	17	*	13
Shear Creep	Imm. After Irradiation	Fell	Fell	Fell	Fell	Fell
	10 Min. After Irradiation	Fell	Fell	Fell	Fell	Fell
Pot Life (hrs.)		>12	>12	>12	>12	>12
Initial 90° Peel Creep (g)		<100	<100	<100	<100	<100
Conversion (%)	Imm. After Irradiation	0	0	0	>95	18
	12 Hrs. After Irradiation	0	12	12	>95	28
	24 Hrs. After Irradiation	0	40	40	>95	45
Elongation at Break (%)		Immeasurable	280	35	2	170
Dynamic Tensile Modulus (Pa)		Immeasurable	5.50 × 10 ⁵	6.40 × 10 ⁵	4.40 × 10 ⁵	5.40 × 10 ⁶

*) Failed to combine

As demonstrated in Tables 4 - 6, the adhesive compositions of Examples 1 - 14 exhibit suitably spreadable viscosity, increased adhesive strength and improved cohesion immediately after exposure to a radiation, extended pot life, and sufficient build-up of adhesive strength 7 days after exposure to a radiation.

As can be seen from Tables 4 and 7, the adhesive compositions of Comparative Examples 1, 2, 4 - 6, because of their exclusion of a thixotropic agent (E), and the adhesive composition of Comparative Example 3, because of its exclusion of both the compound (C) having a polymerizable group in a molecule and the compound (D) which is activated when exposed to a radiation to initiate polymerization of a polymerizable groups in the compound (C), exhibit inferior adhesive strength immediately after exposure to a radiation.

EFFECTS OF THE INVENTION

The adhesive composition in accordance with the first invention, prior to exposure to an active energy radiation, i.e., initially exhibits a sufficient flowability to permit easy application thereof on an adherend by hands or by a spreader. When it is exposed to an active energy radiation, the compound (Y) therein is allowed to decompose rapidly and the compound (X) is allowed to crosslink or polymerize. In this instance, because a part of the compound (X) is left

unreacted within a normal spreadable time, the adhesive composition can afford to develop a suitable level of cohesion commensurate with a residual content of the compound (X) and exhibits a degree of tack that eliminates the need of temporary fixing. After termination of exposure to an active energy radiation, the polymerization and cross-linking are allowed to go proceed in the form of a dark reaction. Accordingly, curing is allowed to proceed in a rapid fashion.

As such, the first invention can provide an adhesive composition which exhibits good storage stability, curing characteristics and working properties. Also, the adhesive composition after cure exhibits the superior resistance to impact and creep.

The adhesive composition in accordance with the second invention contains a component that cures in the presence of moisture in the air, a component that develops cohesion by short-time exposure to a radiation, and a thixotropic agent. Accordingly, this adhesive composition is flowable at ordinary state, shows a spreadable viscosity and a long pot life, develops cohesion by short-time exposure to a radiation, eliminates the need of temporary bonding or fixing, suits to a joining process on line, and exhibits superior physical properties, such as impact resistance and creep resistance, after it is applied and then cured.

CLAIMS

1. An adhesive composition characterized as containing a compound (X) having a crosslinkable or polymerizable group and a compound (Y) which is activated when exposed to an active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X) wherein:

said composition has a viscosity at 25 °C of 1 - 10,000,000 cps; a conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation does not exceed 70 %; a conversion of the compound (X) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C is in the range of 50 - 100 %; and after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of 10^5 - 10^9 Pa.

2. The adhesive composition as recited in claim 1, characterized in that the conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation is in the range of 10 - 70 %, and the adhesive composition immediately after its exposure to the active energy radiation has a dynamic shear modulus

in the range of $10^5 - 10^7$ Pa.

3. The adhesive composition as recited in claim 1, characterized in that the conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation does not exceed 30 % and the adhesive composition has a viscosity at 25 °C of 1 - 10,000,000 cps; and

the conversion of the compound (X) after exposure of the adhesive composition to the active energy radiation and subsequent 12-hour aging at 25 °C is in the range of 50 - 100 %.

4. An adhesive composition characterized as containing the following components:

(A) a compound having at least two hydrolyzable silyl groups in a molecule;

(B) a compound which initiates crosslinking of the compound (A);

(C) a compound having a polymerizable group in a molecule;

(D) a compound which is activated by irradiation to initiate polymerization of the polymerizable group in the compound (C); and

(E) a thixotropic agent.

5. The adhesive composition as recited in claim 4, characterized in that the hydrolyzable silyl group in the

compound (A) is a alkoxysilyl group, and the compound (A) is a compound containing the alkoxysilyl group substituted in a polymer selected from polyalkylene glycols and polyolefins.

6. The adhesive composition as recited in claim 4 or 5, characterized in that the polymerizable group in the compound (C) is a free-radically polymerizable group and the compound (D) is a photochemically free-radical generating agent.

7. The adhesive composition as recited in any one of claims 4 - 6, characterized in that the free-radically polymerizable group in the compound (C) is a polymerizable group selected from acryloyl and methacryloyl groups.

8. The adhesive composition as recited in any one of claims 4 - 7, characterized in that the compound (C) contains at least one type of compound (F) containing at least one polymerizable group in a molecule and having a weight average molecular weight of not less than 3,000.

9. The adhesive composition as recited in any one of claims 4 - 8, characterized in that the thixotropic agent (F) is at least one type selected from the group consisting of glass balloons, glass beads, surface-treated calcium carbonates and various silicas.

10. A method of joining members characterized as comprising, in sequence, applying the adhesive composition as recited in any one of claims 1 - 9 to one of the members,

exposing a top surface of the applied adhesive composition layer to an active energy radiation and combining the one member with the other member.

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5 An adhesive composition is provided which is flowable, shows a spreadable viscosity and a long pot life, develops cohesion by short-time exposure to a radiation, eliminates the need of temporary fixing, and exhibits the superior resistance to impact and creep after cure.

10 The adhesive composition contains (X) a compound having a crosslinkable or polymerizable group and (Y) a compound which is activated when exposed to an active energy radiation to generate species that cause crosslinking or polymerization of at least a part of the compound (X); wherein the composition has a viscosity at 25 °C of 1 - 10,000,000 cps, a conversion of the compound (X) immediately after exposure of the adhesive composition to the active energy radiation does not exceed 70 %, a conversion of the compound (X) after exposure of the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C is in the range of 50 - 100 %, and after exposure of 20 the adhesive composition to the active energy radiation and subsequent 24-hour aging at 25 °C, the cured composition has an elongation at break of 10 - 1,000 % and a dynamic tensile modulus in the range of $10^5 - 10^9$ Pa.

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

ADHESIVE COMPOSITION AND JOINING METHOD UTILIZING
THE ADHESIVE COMPOSITION

the specification of which is ☒ attached and/or ☐ was filed on as Application Serial No.

..... and was amended on (if applicable)
☒ international (PCT) application No. PCT/JP00/05694 filed August 24, 2000 and as amended on April 12, 2001 (if any).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NUMBER	DATE OF FILING	PRIORITY CLAIMED UNDER 35 U.S.C. 119
JAPAN	241599/1999	08/27/1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

☐ See attached list for additional prior foreign applications

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION NUMBER	DATE OF FILING	STATUS (Patented, Pending, Abandoned)

(3)

I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Law Offices of Townsend & Banta: Donald E. Townsend, Registration No. 22,069; Teresa J. Banta, Registration No. 34,543; and Donald E. Townsend, Jr., Reg. No. 43,198. Please address all correspondence to the Law Offices of Townsend & Banta, Suite 500, 1225 Eye Street, N.W., Washington, D.C. 20005

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR <u>Takeo Kuroda</u>		INVENTOR'S SIGNATURE <u>Takeo Kuroda</u>	DATE <u>October 31, 2001</u>
RESIDENCE <u>c/o SEKISUI CHEMICAL CO., LTD., 2-1, Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618-8589 JAPAN</u>		CITIZENSHIP <u>JAPAN</u>	
POST OFFICE ADDRESS <u>Same as Residence</u>			
FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>Hiroji Fukui</u>		INVENTOR'S SIGNATURE <u>Hiroji Fukui</u>	DATE <u>October 30, 2001</u>
RESIDENCE <u>c/o SEKISUI CHEMICAL CO., LTD., 2-1, Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618-8589 JAPAN</u>		CITIZENSHIP <u>JAPAN</u>	
POST OFFICE ADDRESS <u>Same as Residence</u>			

Listing of Inventors Continued on Page 2 hereof. ☒ Yes ☐ No

Listing of Inventors Continued from Page 1 of Declaration and Power of Attorney for invention entitled:

ADHESIVE COMPOSITION AND JOINING METHOD UTILIZING THE ADHESIVE COMPOSITION

3-00 FULL NAME OF THIRD JOINT INVENTOR, IF ANY <u>Hideaki Ishizawa</u>		INVENTOR'S SIGNATURE <u>Hideaki Ishizawa</u>		DATE <u>October 30, 2001</u>
RESIDENCE <u>c/o SEKISUI CHEMICAL CO., LTD., 2-1, Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618-8589 JAPAN</u>		CITIZENSHIP <u>gpx</u>		<u>JAPAN</u>
POST OFFICE ADDRESS <u>Same as Residence</u>				
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF NINTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF TENTH JOINT INVENTOR, IF ANY		INVENTOR'S SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				